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TRANSITION METAL CARBENE COMPLEXES(U) NORTH CAROLINA
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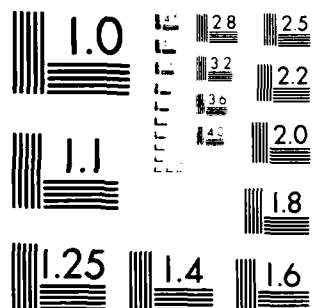
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TRANSITION METAL CARBENE COMPLEXES

FINAL TECHNICAL REPORT

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14 JULY 1984

U. S. ARMY RESEARCH OFFICE

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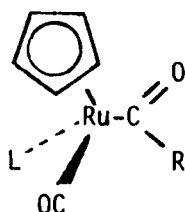
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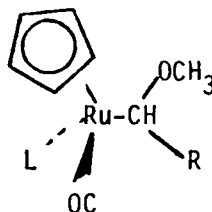
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A. Precursors to Ruthenium Carbene Complexes

A series of acyl ruthenium complexes, 1a-1e, were prepared and converted to their methoxy-derivatives, 2a-2e, to serve as precursors for non-heteroatom-stabilized ruthenium carbene complexes.



1a - 1e



2a - 2e

- a, R = C₆H₅, L = CO
- b, R = p-C₆H₄CH₃, L = CO
- c, R = p-C₆H₄OCH₃, L = CO
- d, R = CH₃, L = CO
- e, R = CH₃, L = P(C₆H₅)₃

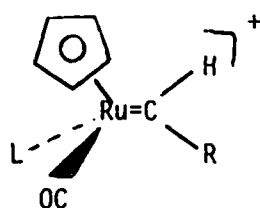
Syntheses of acyl complexes 1a - 1d were accomplished using published procedures. Complex 1e was prepared by reaction of the cationic complex, CpRu(P(C₆H₅)₃)(CO)₂⁺ with methyl Grignard reagent. Yields of all acyl complexes were similar to their iron analogues, ranging from 40 to 75%.

Syntheses of the complexes 2a-2e was best achieved by transformation of the acyl complexes 1a-1e in a manner used to prepare the analogous iron complexes. Complexes 1a-1e were treated with CF₃SO₃CH₃ in CH₂Cl₂, then reduced by NaBH₄ in cold, basic methanol. Although yields of 2a-2e were similar to those obtained for the iron analogues, ruthenium appears to impart enhanced stability. Thus, refluxing these compounds in hexane for five to ten minutes did not lead to significant decomposition.

Complexes 1a-1e and 2a-2e were extensively characterized using IR, ^1H and ^{13}C NMR, and elemental analysis.

B. Ruthenium Carbene Complexes

Complexes 2a-2e were reacted with $\text{CF}_3\text{SO}_3\text{Si}(\text{CH}_3)_3$ in CD_2Cl_2 at low temperatures (-80°C) to yield the first observed ruthenium arylidene complexes. They were easily identified by the characteristic low-field resonances of the carbene protons shown below:



3a - 3e

| Complex | δ H carbene |
|---------|-----------------------|
| 3a | 14.13 |
| 3b | 16.07 |
| 3c | 14.86 |
| 3d | n. o. |
| 3e | 17.62 |

Variable temperature ^1H NMR has previously been used to observe the barrier to aryl rotation about the carbene-carbon and ipso-carbon in aryl substituted iron carbene complexes. Similar measurements were made with 3b and 3c. These are compared with the iron analogs in the following table.

| Ru Compound | R | Δ^G_{rot} | |
|----------------|-----------------------------------|-------------------------|------|
| | | Fe | Ru |
| 3b | $\text{C}_6\text{H}_4\text{CH}_3$ | 10.4 | 10.9 |
| 3c | $\text{C}_6\text{H}_4\text{CH}_3$ | 13.1 | 14.8 |

Ethylidene complex, 3d, could not be observed even at -100°C . Its existence as an unstable species, however, was inferred by cyclopropane formation during attempted generation. On the other hand, replacement of one carbonyl by triphenylphosphine appears to stabilize the ethylidene complex, 3e, markedly. This latter compound was observed to be stable at room temperature, $t_{1/2} > 1$ day. Characterization is incomplete at this writing.

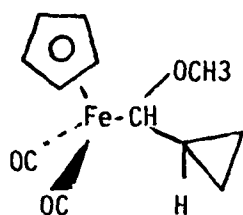
Ruthenium Carbene Transfers

Although carbene complex 3d could not be observed even at -100°C , like its iron analogue it appears to exist as a very unstable species. In situ generation in the presence of styrene results in a 30-40% yield of 2-methyl-1-phenylcyclopropane. Stereochemically, the reaction produces predominantly cis-cyclopropane with the observed ratio cis:trans = 3:1.

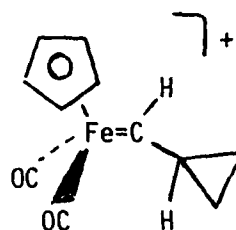
No ethylidene transfers have been attempted using complex 3e.

Iron Carbene Complexes

The preparation of the iron alpha-ether complex, 4, has been described previously described. Most recently this complex has been successfully



4



5

converted to a cyclopropyl carbene complex. Treatment of 4 with $\text{CF}_3\text{SO}_3\text{Si}(\text{CH}_3)_3$ at -80°C generates carbene 5, which was observed by ^1H NMR. Complex 5 is stable to -30°C and is the first alkylidene complex containing a beta-hydrogen to be observed. Warming 5 to room temperature leads to a number of decomposition products which have not been fully characterized. Preliminary results suggest that 5 reacts with styrene to produce 2-phenyl-1-(1,1')bicyclopropyl.

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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Arylidene complexes of ruthenium have been successfully prepared. These complexes possess reasonable stability and undergo cyclopropanation reactions with olefins. Cis-stereochemistry predominates in the latter reactions. A remarkably stable cyclopropyl substituted carbene complex of iron has been prepared. This complex also undergoes cyclopropanation reactions. | | |

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